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THERMAL STUDIES ON NICKEL(II) 4-IODOPYRAZOLE COMPLEXES

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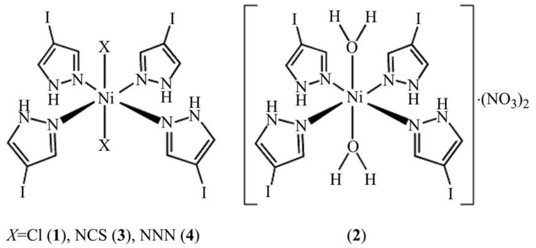
This work describes the synthesis, IR and UV-Vis spectroscopic characterization as well the thermal behavior of the $[NiCl_2(HIPz)_4]·C_3H_6O$ (**1**), $[Ni(H_2O)_2(HIPz)_4](NO_3)_2$ (**2**), $[Ni(NCS)_2(HIPz)_4]$ (**3**) and $[Ni(N_3)_2(HIPz)_4]$ (**4**) (HIPz=4-iodopyrazole) pyrazolyl complexes. TG experiments reveal that the compounds **1**–**4** undergo thermal decomposition in three or four mass loss steps yielding NiO as final residue, which was identified by X-ray powder diffraction.

Keywords: *DSC, 4-iodopyrazole, nickel(II), pseudohalides, TG*

Introduction

The versatility of coordination modes of pyrazolyl ligands together with the potential uses of their complexes as phosphorescent materials [1, 2], CVD source reagents [3], liquid crystals [4], antimicrobial [5] and antitumoral drugs [6, 7] is the subject of intense research. Particularly, Ni(II) pyrazolyl complexes have attracted considerable interest mainly due to their catalytic activities [8, 9] as well their unusual supramolecular architectures [10].

As a part of our investigations on the supramolecular and coordination chemistry of transition metal complexes containing N-based ligands and pseudohalides [11–17], we report herein the synthesis, spectroscopic characterization and the thermal study on the complexes $[NiCl_2(HIPz)_4]·C_3H_6O$ (**1**), $[Ni(H_2O)_2(HIPz)_4](NO_3)_2$ (**2**), $[Ni(NCS)_2(HIPz)_4]$ (**3**) and $[Ni(N_3)_2(HIPz)_4]$ (**4**) (HIPz=4-iodopyrazole) (Scheme 1).



Scheme 1

Experimental

Preparation of the complexes

$[NiCl_2(HIPz)_4]·C_3H_6O$ (**1**) was prepared by the addition of 335 mg (1.73 mmol) of 4-iodopyrazole to a deep green solution containing 100 mg (0.421 mmol) of $NiCl_2·6H_2O$, in 4:1 water/acetone mixture. After stirring for 2 h a blue solution was formed, which was slowly evaporated yielding blue crystals. The crystalline solid was isolated by filtration, washed with acetone and dried under vacuum. The yield was 70%.

$[Ni(H_2O)_2(HIPz)_4](NO_3)_2$ (**2**) complex was obtained by the addition of 273 mg (1.41 mmol) of 4-iodopyrazole to an aqueous solution of $Ni(NO_3)_2·6H_2O$ (100 mg; 0.344 mmol). After 2 h of stirring a blue solution was formed. Blue crystals obtained after the solvent evaporation were isolated by filtration, washed with acetone and dried under vacuum a 50% of yield was obtained.

The $[Ni(NCS)_2(HIPz)_4]$ (**3**) compound was synthesized as follows: to a solution of $NiCl_2·6H_2O$ (100 mg; 0.421 mmol) in 4:1 water/acetone NaSCN (72 mg; 0.888 mmol) in 2 mL of water was dropwise added. After 20 min, 4-iodopyrazole (335 mg, 1.73 mmol) dissolved in 5 mL of acetone was added affording a purple suspension. The stirring was maintained for 2 h and the compound was isolated by filtration washed with acetone and dried under vacuum with a yield of 70%.

$[Ni(N_3)_2(HdmPz)_4]$ (**4**) complex was prepared following the procedure: to a deep green water/acetone (4:1) solution of $NiCl_2·6H_2O$ (100 mg; 0.421 mmol), NaN_3 (57 mg; 0.877 mmol) in 2 mL of water was added. A blue suspension was formed after the addition of 4-iodopyrazole (335 mg; 1.73 mmol) dissolved in 5 mL of acetone. The stirring was maintained for 2 h and the compound was isolated by filtration, washed with acetone and dried under vacuum. Yield was 60%.

Instrumentation

Elemental analyses of carbon, nitrogen and hydrogen were performed on a CE Instruments, model

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EA 1110 – CHNS-O microanalyser. Infrared spectra were recorded on a Nicolet FTIR-Impact 400 spectrophotometer in the spectral range of 4000–400 cm^{-1} using KBr pellets. UV-Vis spectra were obtained on a PerkinElmer Lambda 14P spectrophotometer, in the 190–1100 nm range using $5\cdot10^{-3}$ mol L^{-1} ethanol solutions. Conductivity measurements were perfomed at room temperature in 10^{-3} mol L^{-1} methanol solutions employing a Digimed DM-31 conductometer.

TG and DSC experiments were carried out using a Shimadzu system model TGA-50 and DSC-50, respectively. The TG curves were recorded in flowing dry synthetic air (100 mL min^{-1}) up to 900°C at heating rate of 20°C min^{-1} in platinum sample holders. With the same heating rate was applied in the DSC experiments up to 500°C using aluminum sample holders. X-ray powder diffractograms of the residues were obtained using a Siemens D-5000 diffractometer equipped with a proportional counter and pulse height discriminator. The Bragg–Bretano arrangement was adopted using CuK_α radiation (λ=1.541 Å) and setting of 34 kV and 20 mA. The peaks were identified using PDF base [18].

Results and discussion

The reactions involving nickel(II) salts as precursors carried out under mild conditions afforded new and air-stable coordination compounds whose analytical data (Table 1) agree well with the proposed formulae.

Infrared spectra

The neutral monodentate coordination of the pyrazolyl ligand in **1**–**4** was evidenced by the presence of intense ν_{NH} bands at ca. 3400–3270 cm^{-1} as well by the shift of the bands associated to ring breathing vibrational modes to lower wavenumbers (1520–1506 cm^{-1}) when compared to the free ligand (1533 cm^{-1}) [11–13]. IR experiments also revealed the presence of acetone lattice in **1** by the appearance of the typical ν_{CO} band at 1736 cm^{-1}. The presence of coordinated water molecules in **2** was detected by their characteristic absorptions at 3400 (ν_{OH}), 1637 (δ_{HOH}) and 814 ($\rho_{r(H_2O)}$) cm^{-1}. An intense band centered at 1382 cm^{-1} ($\nu_{as(ONO)}$) in the IR spectrum of **2** strongly suggests the presence of ionic nitrate [19]. In fact, conductivity value of 227 µS cm^{-1} in methanol for **2** is in agreement with 1:2 electrolytes [20]. In the spectra of **3** and **4** the terminal coordination of the pseudohalides was evidenced by the appearance of intense and sharp bands at 2082–2067 cm^{-1} ($\nu_{as(NCS)}$) and 2063 cm^{-1} ($\nu_{as(NNN)}$), respectively [19].

UV-Vis studies

The electron absorption data of **1**–**4** as well their attributions are listed in Table 2. In the spectra bands at ca. 384–400 nm $\{^3A_{2g}\rightarrow{}^3T_{1g}(P)\}$, 618–730 nm $\{^3A_{2g}\rightarrow{}^3T_{1g}(F)\}$ and 1001–1075 nm $\{^3A_{2g}\rightarrow{}^3T_{2g}(F)\}$ association to spin-allowed ligand field transitions were observed, which is typical for Ni(II) octahedral d^8 electron systems [21].

Thermoanalytical studies

TG and DSC curves for **1**–**4** complexes are illustrated in Fig. 1. Table 3 lists the results of the thermal investigations of these compounds together with the assignments of each decomposition stage based on mass calculation. It is worth mentioning that the groups indicated at the right column of the Table 3 do not correspond necessarily to the gaseous final products of decomposition. The TG curves showed that the ther-

Table 1 Melting points (°C) and analytical data of the nickel(II) compounds

Complex	*m.p.*/°C	Carbon/%		Nitrogen/%		Hydrogen/%	
		found	calc.	found	calc.	found	calc.
1	210 dec.	18.83	18.70	11.57	11.63	1.99	1.88
2	102–103	14.80	14.49	13.48	14.08	1.56	1.62
3	170 dec.	17.55	17.69	14.33	14.73	1.29	1.27
4	134 dec.	15.35	15.69	21.18	21.35	1.24	1.32

Table 2 Ligand field transitions in nickel(II) complexes

Complex	λ/nm					
	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$	$\varepsilon/M^{-1}\ cm^{-1}$	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$	$\varepsilon/M^{-1}\ cm^{-1}$	$^3A_{2g}\rightarrow{}^3T_{2g}(F)$	$\varepsilon/M^{-1}\ cm^{-1}$
1	400	11.3	671–730	4.3	1075	2.9
2	396	31.2	665–728	14.2	–	–
3	393	15.4	653–729	6.8	1037	6.8
4	384	51.2	618	22.4	1001	10.7

Table 3 Thermal analysis data for nickel(II) compounds

Complex	Step	ΔT/°C	Δm/%		DSC peaks/°C		Assignment
			obt.	calc.	endo	exo	
1	1	40–121	–7.39	–6.03	84	–	$-C_3H_6O$
	2	121–277	–43.13	–42.27	139, 236	–	–2.10HIPz
	3	277–312	–23.13	–24.16	280	–	–1.20HIPz
	4	312–636	–18.46	–19.79	–	–	–0.70HIPz, $-2Cl^-$, $+0.5O_2$
	residue		7.89	7.75			NiO
2	1	85–280	–49.64	–50.43	94	177, 195	$-2H_2O$, –2.40HIPz
	2	280–452	–24.93	–24.38	–	–	–1.25HIPz
	3	452–601	–18.27	–17.68	–	–	–0.35HIPz, $-2NO_3^-$, $+0.5O_2$
	residue		7.16	7.51			NiO
3	1	136–254	–48.24	–48.96	215	–	–2.40HIPz
	2	254–484	–26.63	–26.52	268	–	–1.30HIPz
	3	484–607	–14.97	–14.97	–	–	–0.30HIPz, $-NCS^-$, $-CN^-$
	4	607–705	–2.64	–1.69	–	–	$-S^{2-}$, $+0.5O_2$
	residue		7.52	7.86			NiO
4	1	92–302	–38.52	–38.00	177	–	–1.80HIPz
	2	302–423	–41.00	–42.23	–	386	–2HIPz
	3	423–497	–11.91	–11.64	–	–	–0.2HIPz, $-2N_3^-$, $+0.5O_2$
	residue		8.57	8.13			NiO

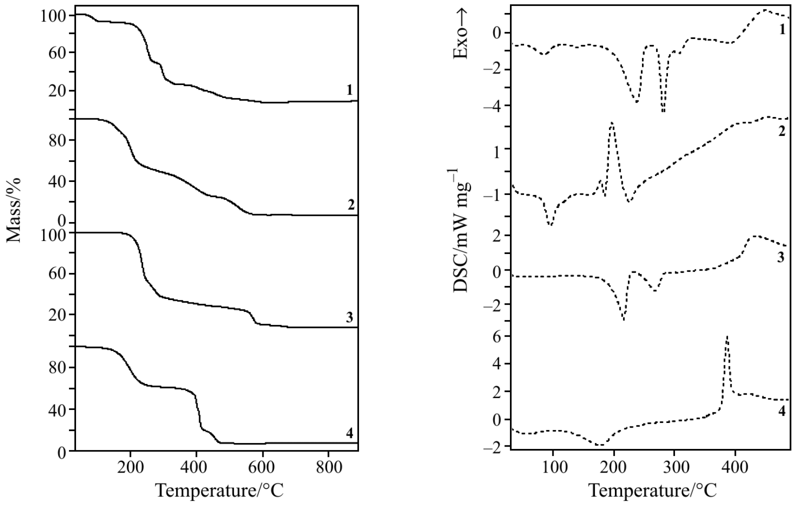

Fig. 1 —— – TG and ··· – DSC curves for the complexes **1**–**4**

mal degradation pattern of **1**–**4** consists of the gradual elimination of the 4-iodopyrazolyl ligands during the initial decomposition steps. For **1**, **2** and **4** complexes the degradation of the anionic groups of the remaining HIPz ligands and the uptake of O_2 occur in the last mass loss affording NiO as a final residue (ASTM 78-0643) [10]. With regard to the thermal behavior of **3**, NiS (ASTM 77-1624) [18] is formed after the decomposition of the ligands. A further increase of temperature up to 705°C results in the last mass loss characterized by the conversion of NiS to NiO (ASTM 78-0643) [18]. The DSC curves of **1**–**4** show a series of signals associated to endothermic and exothermic decomposition processes. According to the DSC curve of **1** (Fig. 1), the lattice acetone is lost at 84°C, yielding $[NiCl_2(HIPz)_4]$ in its anhydrous form, which is thermally stable up to 121°C.

Conclusions

This work describes the synthesis, spectroscopic characterization and thermal studies of the new nickel(II) pyrazolyl complexes $[NiCl_2(HIPz)_4]\cdot C_3H_6O$ (**1**), $[Ni(H_2O)_2(HIPz)_4](NO_3)_2$ (**2**), $[Ni(NCS)_2(HIPz)_4]$ (**3**) and $[Ni(N_3)_2(HIPz)_4]$ (**4**). From the inspection of TG curves of the neutral $[NiX_2(HIPz)_4]$ complexes $\{X{=}Cl^-$ (**1**); NCS^- (**3**); NNN^- (**4**)$\}$, it is noticed that the stability varies according to the anionic groups following the $NCS^- > Cl^- > NNN^-$ order. The lowest thermal stability of **4** is probably ascribed to the known explosive nature of inorganic azides [22].

Acknowledgements

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